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STUDY OF THE MAGNETIC FIELD DEPENDENCE OF THE MOLECULAR NI (CO)--ETC(U)
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ANNUAL RESEARCH REPORT

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Study of the Magnetic Field Dependence
of the Molecular Ni(CO)₄ Formation Rate

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Abstract

Initial work on the dependence of the nickel carbonylation rate on time, temperature and magnetic field has been completed and a manuscript describing this work in detail has been accepted for publication. Our current effort is in the study of the magnetic phase dependence of chemical activity (The Hedvall Effect). The nickel carbonylation reaction offers an ideal system for the study of this effect. One of the advantages of this system is the availability of Ni_{1-x}Cu_x alloys over the entire composition range $0 < x < 1$, thereby making accessible a wide range of Curie temperatures. Our preliminary results on this system show that the ferromagnetic to paramagnetic transition leads to a large change in the activation energy for the carbonylation reaction. Auger measurements confirm that the chemical reaction emphasizes the surface Ni atoms while the activation energy emphasizes the bulk Ni.

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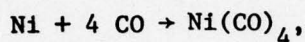
Grant # AFOSR-77-3130

Study of the Magnetic Field Dependence of the Molecular $\text{Ni}(\text{CO})_4$ Formation Rate

M.S. Dresselhaus, M.I.T., Principal Investigator

I. INTRODUCTION

The first nine months of this grant year were spent in completing our study of the carbonylation reaction on a metallic nickel surface,



as a function of time, temperature, magnetic field, and surface preparation. This effort has been described in detail in our previous annual report. We have presented our results in detail in Appendix A, which is a preprint of a paper accepted for publication in Surface Science. Therefore, we will summarize this portion of the work briefly in this year's annual report.

Instead, this report will emphasize our activities since July 1, 1978, when we started serious work on the Hedvall Effect. Our preliminary work on the Hedvall Effect has revealed important results on the connection between the magnetic state of chemical reacting species and their chemical activity. It is our intention to emphasize this work during the coming year, when we will develop these ideas in detail.

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II. Brief Summary of the Dependence of Ni(CO)_4 Formation Rate on Time, Temperature and Magnetic Field

The interaction of Ni with CO gas to produce Ni(CO)_4 at 1 atmosphere pressure has been studied as a function of time, temperature ($25 < T < 95^\circ\text{C}$) and externally applied magnetic field ($H \leq 500 \text{ Oe}$). Our results on the time and temperature dependence of this reaction rate (See Figs. 2A and 3A) are in qualitative agreement with the results of Trivin and Bonnetain, though our results on the temperature dependence are in disagreement with data reported by Goldberger and by Krinchik et al. Of particular interest is our failure to observe any significant magnetic field dependence of the carbonylation rate in this temperature range, in sharp contradiction with results previously reported by Krinchik et al. In the temperature range $25 < T < 95^\circ\text{C}$, the activation energy for the carbonylation reaction is found to be $0.21 \pm 0.05 \text{ eV}$, independent of magnetic field. A detailed discussion of this work appears in Appendix A, which has been accepted for publication in Surface Science.

III. Magnetic Phase Dependence of Chemical Reactions

It has already been demonstrated that the reaction rate for a number of chemical reactions undergoes a discontinuous change as the temperature is increased across T_c , so that a transition is made from a magnetically ordered state (ferromagnetic, antiferromagnetic) to a magnetically disordered state (paramagnetic, diamagnetic). An example of this discontinuous increase in reaction rate is shown in Fig.1 for Ni oxidation (Sales and Maple, 1977). This effect, known as the Hedvall Effect, was discovered in 1935 in the context of catalytic chemical reactions. In the intervening years, this effect has been studied on a small number of catalytic reactions. We show here that the $Ni(CO)_4$ system offers particular advantages for the study of this effect. Our preliminary results indicate that for magnetic materials the chemical reaction rate (which predominantly involves surface species) depends on the exchange energy (a bulk phenomenon). Because of the fundamental significance of this observation, we are now focussing our full effort for the coming year on a detailed study of these phenomena, as described below.

The nickel carbonylation reaction is ideally suited for the study of the connection between the magnetic state of the reacting materials and their chemical activity for the following reasons. Firstly, since $Ni(CO)_4$ is a gas, the reaction product leaves the surface after formation, leaving unreacted metallic atoms on the surface for subsequent reaction with the incoming CO gas. Secondly, Ni forms a simple substitutional alloy with Cu, $Ni_{1-x}Cu_x$ over the entire composition range x , thereby allowing linear variation of the Curie temperature from 631K for $x = 0$ (pure Ni) to 0K for $x = .56$. Thirdly, for temperatures high enough so that $Ni(CO)_4$ is readily formed, but low enough so that $Ni(CO)_4$ is not decomposed back to Ni and CO, the reaction of CO with the $Ni_{1-x}Cu_x$ alloy is limited to reaction with Ni and not with Cu. Thus, for the temperature range over which the nickel carbonylation rate is conveniently studied, $280 < T < 440K$, the alloying of Ni with Cu provides a means for variation of

the Curie temperature over this temperature range, with $T_c \approx 280\text{K}$ for $x = .31$ and $T_c \approx 440\text{K}$ for $x = .18$. Furthermore, there is only one magnetically ordered species in the nickel carbonylation reaction, namely ferromagnetic Ni, in contrast with the situation in Fig. 1 for the oxidation of Ni (previously studied by Uhlig, and later by Sales and Maple) where the reaction product is antiferromagnetic NiO which adheres to the surface. It is also of interest that for the carbonylation reaction, Ni can be either ferromagnetic or paramagnetic, while $\text{Ni}(\text{CO})_4$ is diamagnetic. (For convenience in the following discussion we will use the following notation: $T_{\min} = 280\text{K}$, $T_{\max} = 440\text{K}$ to denote the carbonylation temperature range).

In this study we have used the same basic system that was designed to measure the time, temperature and magnetic field dependence of the nickel carbonylation rate (see Fig. 1 of Appendix A). For the Hedvall Effect studies, the sample is a disc of $\text{Ni}_{1-x}\text{Cu}_x$ ($0 \leq x < 1$) and the same surface treatment as described in Appendix A (p. 4A) is used to activate the sample surface prior to the carbonylation reaction.

The carbonylation reaction with the $\text{Ni}_{1-x}\text{Cu}_x$ alloys differs from that with pure nickel insofar as the reaction in the alloy system exhibits an exponential time decay $e^{-t/\tau}$ associated with the depletion of Ni from the surface. Our on-line photoionization detection system conveniently provides this decay rate which is typically monitored for ≈ 10 minutes at constant temperature. The temperature dependence of the carbonylation rate is then found by measuring the reaction rate at a series of temperatures. In making this measurement, we note the change in reaction rate on switching from temperature T_i to T_f and then correct for the exponential time decay while the system is at T_i and at T_f . These results are then plotted in an Arrhenius plot $\ln R$ vs. $1/T$ to find the activation energy ΔE for the reaction ($R \sim e^{-\Delta E/kT}$). For copper concentrations such that the sample is ferromagnetic throughout the temperature range for which the carbonylation reaction is measured

(e.g. $x = 0$ where $T_c \gg T_{max}$), the $\ln R$ vs $1/T$ data fit an Arrhenius plot with a single activation energy. A single activation energy is also found for samples that are paramagnetic between T_{min} and T_{max} . In contrast, when T_c falls within the temperature range over which the carbonylation reaction is measured ($T_{min} < T_c < T_{max}$), the $\ln R$ vs. $1/T$ data exhibit two activation energies, one for the ferromagnetic region, a second for the paramagnetic region. For example for $x = .30$, the results of Fig. 2 show that $\Delta E^{para} = .17\text{eV}$, while $\Delta E^{ferro} = .34\text{eV}$. From these measurements of the temperature dependence of R , we can plot as a function of x (the atomic % Cu) the activation energies ΔE^{para} and ΔE^{ferro} for the ferromagnetic and paramagnetic phases, as shown in Fig. 3. An extrapolation of the data on the "paramagnetic" curve to low x and on the ferromagnetic curve to high x is consistent with the two limiting cases of interest:

for $x = 0$;

$$\Delta E^{para} - \Delta E^{ferro} = \text{Exchange energy for pure Ni (0.364eV)}$$

for $x = 0.56$ (where $T_c = 0$);

$$\Delta E^{para} - \Delta E^{ferro} = 0.$$

These observations suggest that the difference in activation energies ($\Delta E^{para} - \Delta E^{ferro}$) at Cu concentration x gives a direct measurement of the exchange energy for that concentration.

This connection between the exchange energy for the magnetic state and the activation energies for a chemical reaction can be understood on the basis of the following elementary argument. The transition to the ferromagnetic state is accompanied by the transfer of electrons from the spin up band to the spin down band, completely filling the spin down band and leaving the spin-up band with $\sim .54$ holes/Ni ion. This transfer of electrons result in

a lowering of the Fermi level, so that more energy is required when the Ni is in the ferromagnetic rather than the paramagnetic state to modify the electronic configuration (and thereby form a chemical bond).

To establish that the activation energies thus measured are characteristic of the bulk alloy concentration, repeated determinations were made of the activation energies for a given $\text{Ni}_{1-x}\text{Cu}_x$ sample, during a time period over which the reaction rate dropped in absolute value by an order of magnitude. It is significant that the activation energies measured in this way are independent of the absolute magnitude of the reaction rates. After heat treatment to reactivate the nickel surface, the reaction rate returned to approximately the initial value and again no change in the activation energies was found.

Auger analysis of the surface composition of the $x = .30$ sample before and after reaction using the 920 eV line for Cu and the 848 eV line for Ni indicated a large depletion of the Ni atoms in the first few monolayers. This analysis is being made more quantitative using the 105 eV line for Cu and the 102 eV line for Ni, taking advantage of the dependence of the penetration depth on the energy of the Auger electrons. The Auger analysis will allow us to determine the Ni and Cu composition (1) on the surface (first monolayer) using the low energy Auger electrons and (2) within several monolayers of the surface using the higher energy Auger electrons. Our preliminary work shows that the surface Ni atoms are most important in determining the magnitude of the reaction rate, though the activation energy for the carbonylation reaction is more sensitive to the bulk concentration.

We are now initiating a series of careful temperature measurements on a number of samples covering a range of Cu concentrations to obtain quantitative data for Fig. 3. Further improvements are also being made on our techniques for Auger spectroscopy measurements to characterize the Ni/Cu concentration as a function of penetration into the first few monolayers.

FIGURE CAPTIONS

- Fig. 1 Rate of nickel oxidation vs. $1/T$ in the region of the Curie temperature for nickel (631K). An abrupt change in the slope of the reaction rate curve is found at T_c . The change in activation energy is $\Delta E^{\text{ferro}} = 61$ kcal/mole, $\Delta E^{\text{para}} = 36.8$ kcal/mole. (After Sales and Maple, Phys. Rev. Lett. 39,1636 (1977)).
- Fig. 2 Plot of $\ln R$ vs. $1/T$ for the nickel carbonylation reaction in a $\text{Ni}_{.70}\text{Cu}_{.30}$ sample. An abrupt change in activation energy from $\Delta E^{\text{ferro}} = .34\text{eV}$ to $\Delta E^{\text{para}} = .17\text{eV}$ is found near the Curie temperature.
- Fig. 3 Plot of activation energy ΔE^{ferro} and ΔE^{para} vs. x for a series of $\text{Ni}_{1-x}\text{Cu}_x$ samples. We note that $[\Delta E^{\text{ferro}} - \Delta E^{\text{para}}] \rightarrow 0$ as $T_c \rightarrow 0$ and that for $x = 0$ (pure nickel) $[\Delta E^{\text{ferro}} - \Delta E^{\text{para}}] =$ exchange energy for Ni. Work is in progress to obtain the quantitative dependence of ΔE^{ferro} and ΔE^{para} on x .

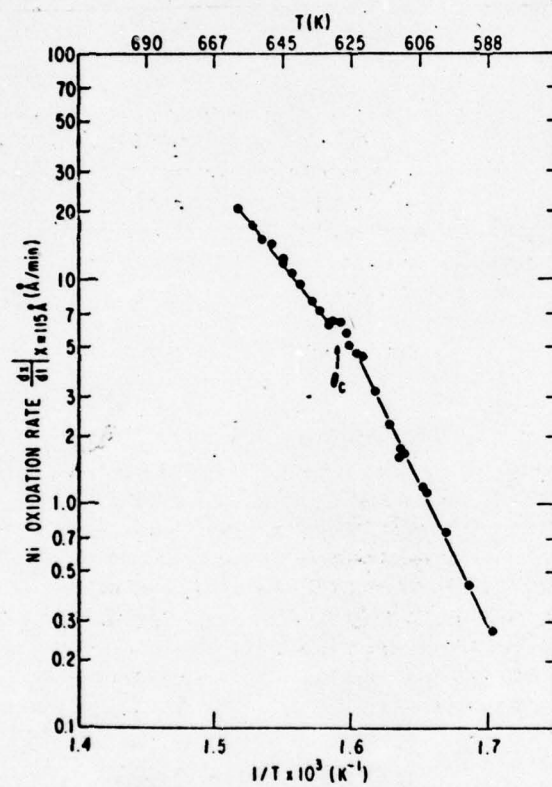


Fig. 1

Carbonylation Rate R for $\text{Ni}_{.70}\text{Cu}_{.30}$

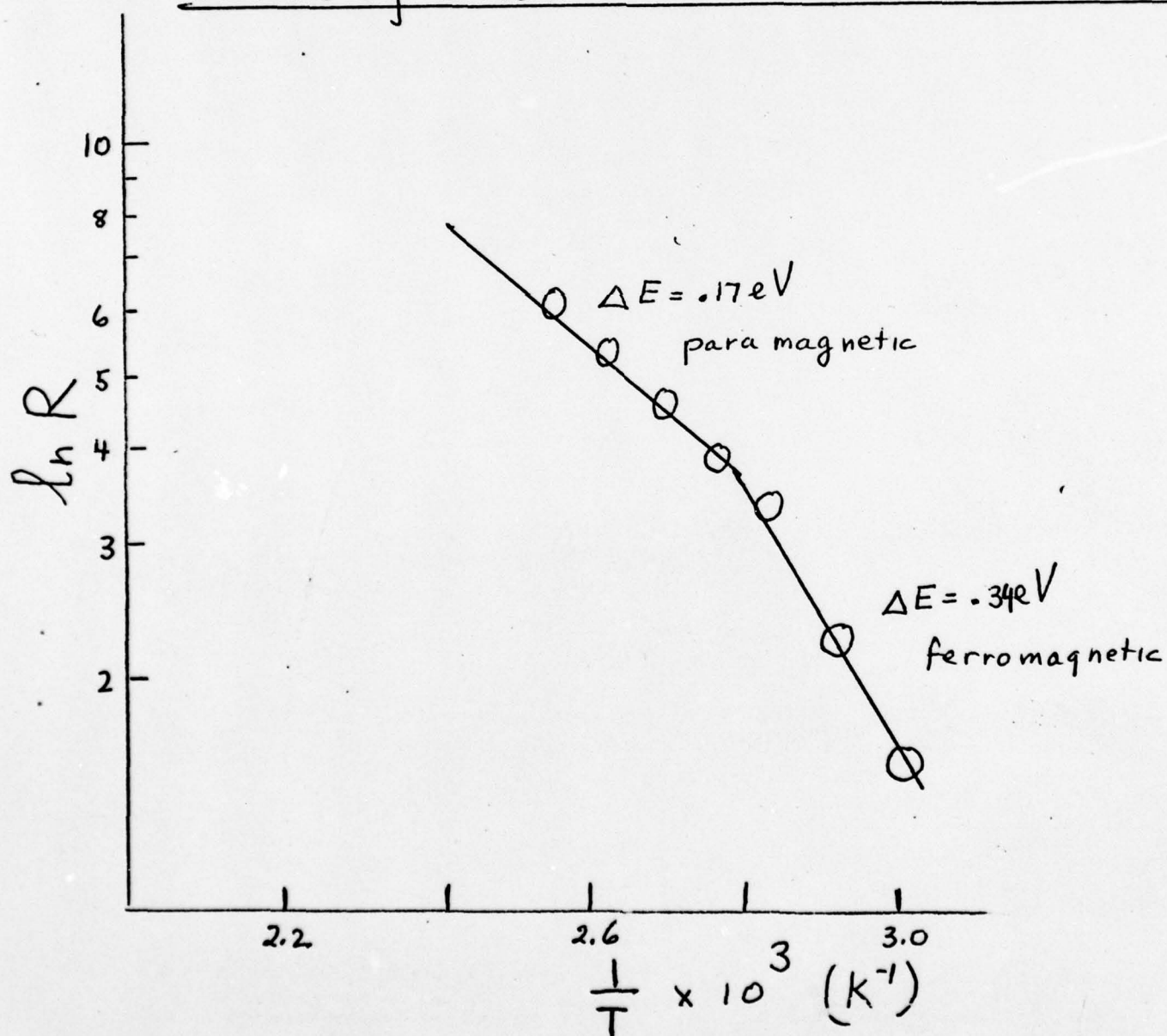


Fig. 2

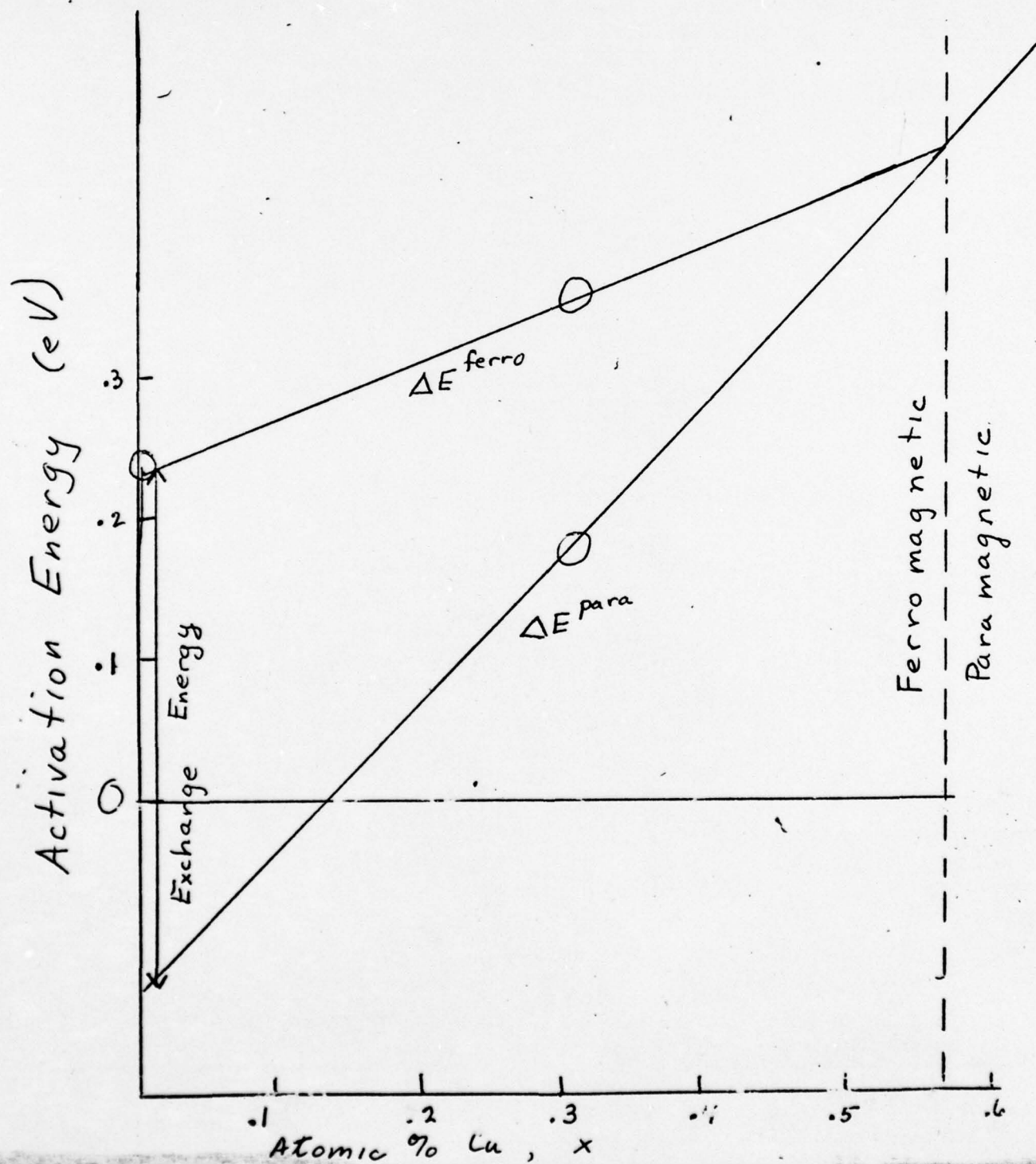


Fig. 3

On the Possible Magnetic Field Dependence
of the Nickel Carbonylation Rate

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ABSTRACT

The interaction of Ni with CO gas to produce $\text{Ni}(\text{CO})_4$ at 1 atmosphere pressure, has been studied as a function of time, temperature ($25 < T < 95^\circ\text{C}$) and externally applied magnetic field ($H \leq 500 \text{ Oe}$). We find no significant magnetic field dependence of the nickel carbonylation rate, in sharp contrast with results previously reported by Krinchik, et al. The activation energy for this reaction is found to be $0.21 \pm 0.05 \text{ eV}$ independent of magnetic field.

On the Possible Magnetic Field Dependence
of the Nickel Carbonylation Rate

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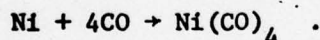
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1. Introduction

During the last few years extensive effort has been devoted to the experimental and theoretical study of the chemisorption of simple molecules on the surfaces of metals and semiconductors [1-5]. These experiments and the resulting theories have generally dealt with the low coverage regime where the adsorbed molecules do not interact with each other. In contrast, the work reported here focusses on the high coverage regime, which is the regime of importance for catalytic surface reactions [6]. The implications of the results in the low coverage regime on behavior in the high coverage regime has not been well established.

The particular reaction that is addressed in this work is the chemisorption of CO on a nickel surface, one of the most extensively studied reactions in the low coverage regime. However, above 5mm CO pressure which is the high coverage regime, CO reacts with Ni to form $\text{Ni}(\text{CO})_4$ [7]



We report here studies of the reaction rate as a function of time, temperature ($25 < T < 95$ C) and externally applied magnetic field ($H \leq 500$ Oe). This reaction has recently attracted considerable attention because of reports that the nickel carbonylation rate can be greatly enhanced

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§ IBM predoctoral fellow.

by the application of weak magnetic fields and that this magnetic field dependence is oscillatory [8-11].

The nickel carbonylation reaction is particularly interesting with regard to possible magnetic field dependence both from a practical and a theoretical point of view. From the practical side, nickel carbonylation is an intermediate step in the commercial purification of nickel [12]. Thus any mechanism which could significantly enhance this reaction rate could have commercial impact. Furthermore, because of the extreme toxicity [13,14] of Ni(CO)_4 , any significant enhancement in its formation rate is of importance to the setting of occupational safety standards for toxic materials. From a theoretical point of view, nickel is a ferromagnetic material with an unfilled 3d-band while Ni(CO)_4 is diamagnetic, with a fully occupied 3d level. This major difference in the magnetic properties of the reagents before and after the chemical reaction suggests that the nickel carbonylation reaction is one which would emphasize magnetic field dependent phenomena.

Since the nickel carbonylation reaction has been reported to be very sensitive to temperature [11,15], magnetic field [8-11] and previous surface preparation [12], a convenient on-line detection system was developed for the study of the dependence of this reaction on these various parameters. A summary of the experimental procedures is given in Section 2, and followed by the results in Section 3.

2. Experimental Procedure

Because of the dependence of the nickel carbonylation rate on several interrelated parameters, convenient on-line detection is highly desirable. The design of an on-line system is however constrained by several factors. Firstly, it is well-known that Ni(CO)_4 is extremely toxic [13,14], and for

this reason we tried to work in the regime of low reaction yields ($\lesssim 2\mu\text{g}/\text{min}$). Thus high sensitivity in the ppb to ppm range was required for the detection system. The second constraining factor on the detector system is associated with the small quantity of $\text{Ni}(\text{CO})_4$ that must be detected in a huge CO background ($\sim 10^6$ greater concentration of CO relative to that of $\text{Ni}(\text{CO})_4$). Thus the detection system must be designed to be highly sensitive to $\text{Ni}(\text{CO})_4$ while discriminating sensitively against CO.

To meet these constraints, a photoionization detector (PID) was used to detect $\text{Ni}(\text{CO})_4$ [16]. This instrument consists of a H_2 ultraviolet light source providing photons of 10.2eV energy. Since the photoionization energy of $\text{Ni}(\text{CO})_4$ is 8.28eV while that for H_2 and CO are 15.42 and 14.01eV respectively, the detector only responds to $\text{Ni}(\text{CO})_4$ (in the ppm range) in a huge CO background.

This detector is central to the system (shown schematically in fig.1) that was set up to study the nickel carbonylation process. Since the carbonylation reaction is extremely sensitive to trace impurities [11], high purity gases are used in all parts of the system shown in fig.1. Even the highest purity CO that is commercially available in gas cylinders has trace concentrations of $\text{Ni}(\text{CO})_4$. To remove these trace concentrations a copper trap heated to 300 C and a cold trap (-100 C) have been incorporated into the system (see fig.1A). The heat trap decomposes $\text{Ni}(\text{CO})_4$ while the cold trap freezes the gas. To remove trace concentrations of CO_2 an Ascarite trap is also inserted in the gas line. The operation of the system and the purity of the gas admitted to the reaction chamber are checked by the response of the photoionization detector when the reaction chamber is by-passed (see fig.1A).

The reaction was carried out with a variety of nickel samples in the

form of polycrystalline nickel rod, nickel discs, single crystal nickel samples and nickel coated on glass beads, all samples starting with nickel of 99.9 to 99.99% purity. To obtain flat surfaces, the samples were first mechanically polished with diamond paste and aluminum oxide powder. This procedure was then followed by chemical cleaning [17]. These mechanical and chemical procedures were used for initial preparation of the sample surfaces.

Each sample was then heat treated at 400 C in a stream of hydrogen for 4 hours in a vycor reaction chamber placed between the poles of an electromagnet. The necessary heat is provided by an oven which is placed around the reaction chamber. The hydrogen gas used to reduce the nickel surface is of the highest commercially available purity. As shown in fig. 1 this hydrogen gas is passed through a gas purifier and the flow rate is held at 200cc/min during the reduction reaction. After a 4 hour heat treatment, the sample is cooled down and brought to a steady temperature by circulating temperature-controlled water or oil through the walls of the oven surrounding the reaction chamber. After this hydrogen reduction procedure is completed, the hydrogen gas is shut off and CO (200cc/min) is introduced into the system. At the end of the run, the sample is kept in the reaction chamber under a hydrogen or helium environment (see fig. 1A). The next run is carried out without opening the system; in this case the initial mechanical and chemical surface preparation procedures are omitted and only the hydrogen reduction heat treatment is employed. With these procedures fully reproducible results were achieved.

The system shown in fig. 1 permits on-line measurement of the nickel carbonyl formation rate as a function of temperature, magnetic field and CO flow rate. The system permits both control and measurement of these parameters. A typical value for the Ni(CO)_4 formation under steady state

conditions at 50 C is 2 μ g/min. Although the photoionization detector can detect trace amounts of Ni(CO)₄ in a large background of CO, the photoionization response is not specific to Ni(CO)₄. For this reason, the photoionization detector is calibrated against two detection systems that are specific to Ni(CO)₄. For this purpose, effluent gas samples are bubbled through a solution of ethyl alcohol and iodine and are collected (see fig.1A). These solutions are subsequently tested for nickel content using the colorimetric [14] or atomic absorption techniques [18]. Since the colorimetric and atomic absorption techniques both depend on the collection of effluent gas samples, time dependent measurements are very difficult to carry out with these techniques. In the context of the present work, both of these techniques were used as calibration standards when a new experimental technique was instituted or a new phenomenon was observed. In addition, the response of the photoionization detector was periodically checked against calibrated quantities of C₄H₈ in air (see fig.1). Because of the extreme sensitivity of the nickel carbonylation reaction to trace amounts of oxygen [11], the various gases used in the experiment were checked for oxygen content by an oxygen analyzer. This instrument was in turn calibrated against a known concentration of O₂ in N₂ (see fig.1A).

A vycor reaction chamber was used to avoid contamination in carrying out the nickel carbonylation reaction; for example the use of a stainless steel reaction chamber could result in the formation of iron carbonyl [19], which would also be detected by the FID. For similar reasons, we avoided using nickel plated parts in our system, so that the Ni sample would be the only nickel seen by the CO gas stream.

A magnetic field up to 500 Oe was provided by a solenoid and a Varian electromagnet with homogeneities better than 1%. This degree of homogeneity

is required to look for oscillations with periodicities comparable to those reported by Krinchik et al [8-11].

3. Results

We now report our results for the dependence of the $\text{Ni}(\text{CO})_4$ formation rate on time, temperature and magnetic field. As shown in Fig.2A, on interacting CO with a hydrogen treated nickel sample, the rate of $\text{Ni}(\text{CO})_4$ formation initially increases rapidly and then slowly decays to a steady state value. The initial delay after the introduction of CO gas into the system corresponds to the time needed to sweep the H_2 gas from the system. Colorimetric and atomic absorption tests on the effluent gas samples have confirmed that the initial peak in the reaction rate, shown in fig.2A does indeed correspond to $\text{Ni}(\text{CO})_4$. Similar time dependent data have been observed with a variety of different nickel samples and under various operating conditions, including variation of sample temperature and externally applied magnetic field. These results are discussed more fully below.

We have carefully checked that the transient behavior in fig.2 is not instrument-related. We attribute the drop in the reaction rate during the first few minutes to a rapid decrease in the number of activated reaction sites on the nickel sample. After about 20 minutes the reaction rate R approaches a constant value R_∞ which is fully reproducible. We have observed that trace impurities in the system cause a generally lower value for R_∞ and a continued decrease in R for time $t > 20$ min. Both the magnitude of the carbonylation rate and its constancy with time after the initial rapid drop indicates that surface poisoning of our nickel samples is not severe.

Similar time-dependent behavior for the nickel carbonylation rate was observed by Trivin et al [20] who studied this reaction as a function of temperature using Ni powder and a spectroscopic on-line detection system.

(Their measurements [20] however did not include any studies of the magnetic field dependence of this reaction.) Our measurements show that within experimental error the time dependence of the reaction is not sensitive to whether the reaction is initiated in zero magnetic field or in the presence of an external magnetic field for $H < 500$ Oe. Nor is the time dependence curve (fig.2A) sensitive to the application of a magnetic field during the course of the reaction. Thus, fig.2 also describes our results in the presence of an externally applied magnetic field. Because of the reproducibility of R_{∞} under similar experimental conditions, it is this quantity that is considered in studying the dependence of the nickel carbonylation rate on external parameters. Our results of fig.2A show that if the Ni(CO)_4 detection scheme should involve time averaging (and not be on-line) then data collection should start only after the initial transient period is over (~ 20 min. for our system).

The dependence of the Ni(CO)_4 formation rate on temperature is shown in fig.3A where $\ln \tilde{R}$ vs $1/T$ is plotted. In constructing this figure \tilde{R} denotes the carbonylation rate normalized to room temperature, $\tilde{R} \equiv R_{\infty}/R_{\infty}^{300}$. In the temperature range $300 < T < 370\text{K}$, a monotonic increase in R_{∞} with T is observed, in qualitative agreement with results reported by Trivin et al [20]. It is also significant that our reaction rate data are consistent with an exponential temperature dependence as is illustrated in fig.3A. When interpreted as a catalyzed activation process, the Arrhenius plot of fig.3A yields an activation energy of $0.21 \pm 0.05\text{eV}$ which is of the order of magnitude of surface exchange energies for magnetic systems.

On the other hand, the data reported by Krinchik [11] and Goldberger [15] indicate that the temperature dependence of the reaction rate has a maximum at 75°C . The reasons for this discrepancy with our data are not known to us.

It may be noted that neither Krinchik nor Goldberger used on-line techniques to monitor their reaction rates, so that their measurements correspond to a time average (e.g. over a 5 min. period) of actual reaction rates.

Our observations of the magnetic field dependence of the nickel carbonylation rate are shown in fig.4aA for a variety of nickel samples (single crystal, polycrystalline rods and discs, and nickel coated glass beads). No striking magnetic field dependence of the $\text{Ni}(\text{CO})_4$ formation rate was observed for magnetic fields $H \leq 500$ Oe. These measurements were made for a variety of temperatures and orientations of the samples and of the magnetic fields. For each measurement the normalization was made to zero magnetic field at that temperature. Both homogeneous and inhomogeneous magnetic fields were applied to the samples. As mentioned above, the application of magnetic fields $H < 500$ Oe yielded no significant influence on the temperature and time dependence of the reaction rate. A search for a magnetic field dependence of the nickel carbonylation rate has also been made by Groff [19] and Crabtree [21].

In conflict with the data in Fig.4aA are the highly magnetic field dependent nickel carbonylation rates reported by Krinchik et al [8-11] using a variety of different types of nickel samples, including single crystals, polycrystalline materials and powders. Of the many field dependent traces shown in their work we have selected one trace (fig.4bA) covering the same magnetic field range as shown in fig.4aA. For each type of nickel material, these authors report that the presence of a small externally applied magnetic field (≤ 3 kOe) significantly alters the reaction rate. At room temperature the reaction rate is claimed to change by as much as a factor of 6, and at 70 C by as much as a factor of 40. With single crystal nickel, these authors found the rate to oscillate as a function of applied H.

(See Fig. 4cA taken at 20 C).

The reason for the discrepancy between our data and those reported by Krinchik et al [8-11] is not understood. It is of interest to note in this connection that magnetic interaction energies $\mu_B H$ at 500 Oe (where μ_B = Bohr magneton) are $< 10^{-5}$ eV while the thermal activation energy of fig. 3A is ~ 0.2 eV. It is therefore difficult to see why such low fields should have a significant effect on the catalytic activation energy.

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Figure Captions

Fig.1A- Schematic diagram for the nickel carbonylation system. The nickel sample is contained in the vycor reaction chamber and can be heated to 400 C by the oven. The bath provides the constant temperature environment for reacting Ni with CO. The $\text{Ni}(\text{CO})_4$ formed is absorbed in the alcohol/iodine solution for disposal or analysis for nickel content. C_4H_8 and O_2 gases are used to calibrate the photoionization detector and the oxygen analyser respectively.

Fig.2A- Plot of nickel carbonylation rate R vs time. After an initial heat treatment of the nickel sample at 400 C for 4 hours in a stream of hydrogen gas, CO gas is introduced. The zero on the time scale denotes the onset of $\text{Ni}(\text{CO})_4$ detection after the time ($\sim 2\text{min}$) needed to sweep the H_2 gas from the system. After about 20 minutes a constant reaction rate denoted by R_∞ is found.

Fig.3A- The temperature dependence of the nickel carbonylation rate R_∞ (see Fig.2A) at $H = 0$ presented as $\ln \tilde{R} = \ln(R_\infty/R_\infty^{300})$ vs $1/T$ where the normalization of the temperature dependent rate is to room temperature $T = 300\text{K}$. This Arrhenius plot yields an activation energy of 0.21eV. Though these data were taken on a polycrystalline Ni sample, similar results are obtained on single crystal nickel and on nickel powder samples.

Fig.4A- (a) The magnetic field dependence of the nickel carbonylation rate R plotted as $R_\infty(H)/R_\infty(0)$ vs H , where $R_\infty(0)$ is the reaction rate at $H = 0$.

(b) Nickel carbonylation rate $R[\mu\text{g g}^{-1} \text{min}^{-1}]$ for Ni powder reported for the same magnetic field range as (a) by Kipnis, et al in ref.[8]

(c) Oscillatory magnetic field dependence of the nickel carbonylation rate $R[\mu\text{g cm}^{-2} \text{min}^{-1}]$ in a single crystal nickel sample at 20C as reported by Krinchik et al in ref.[11].

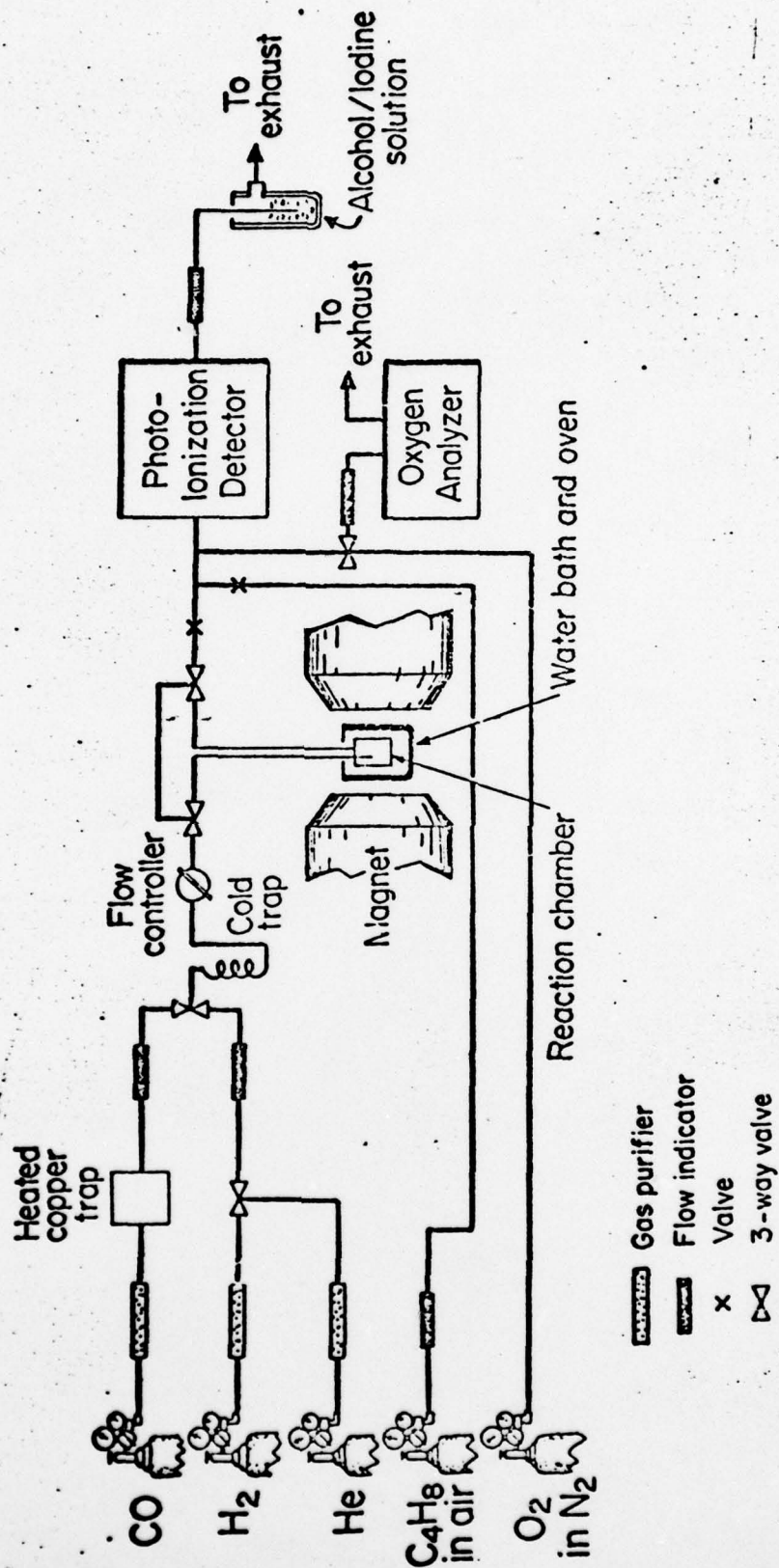


Fig. 1A

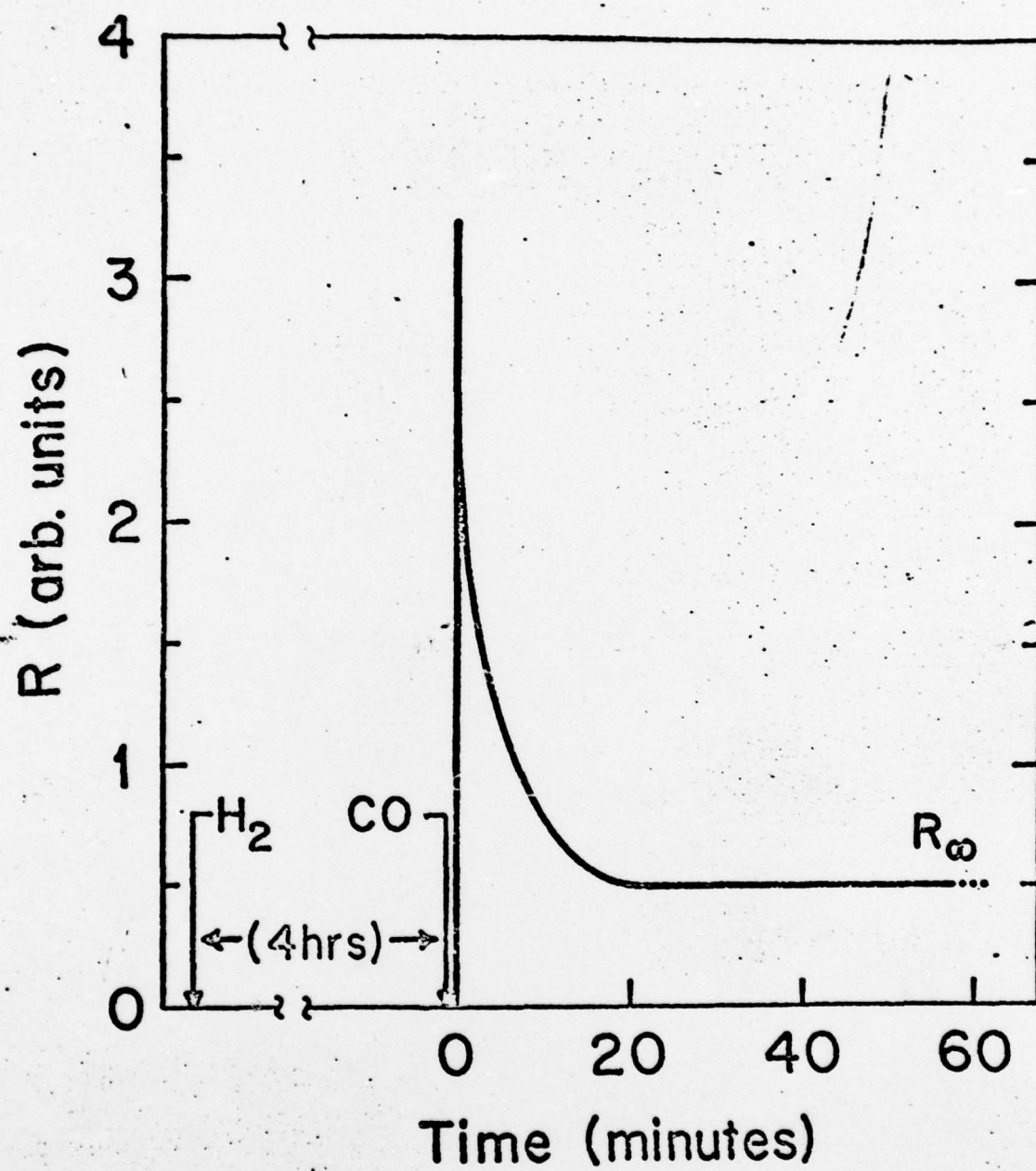


Fig. 2A

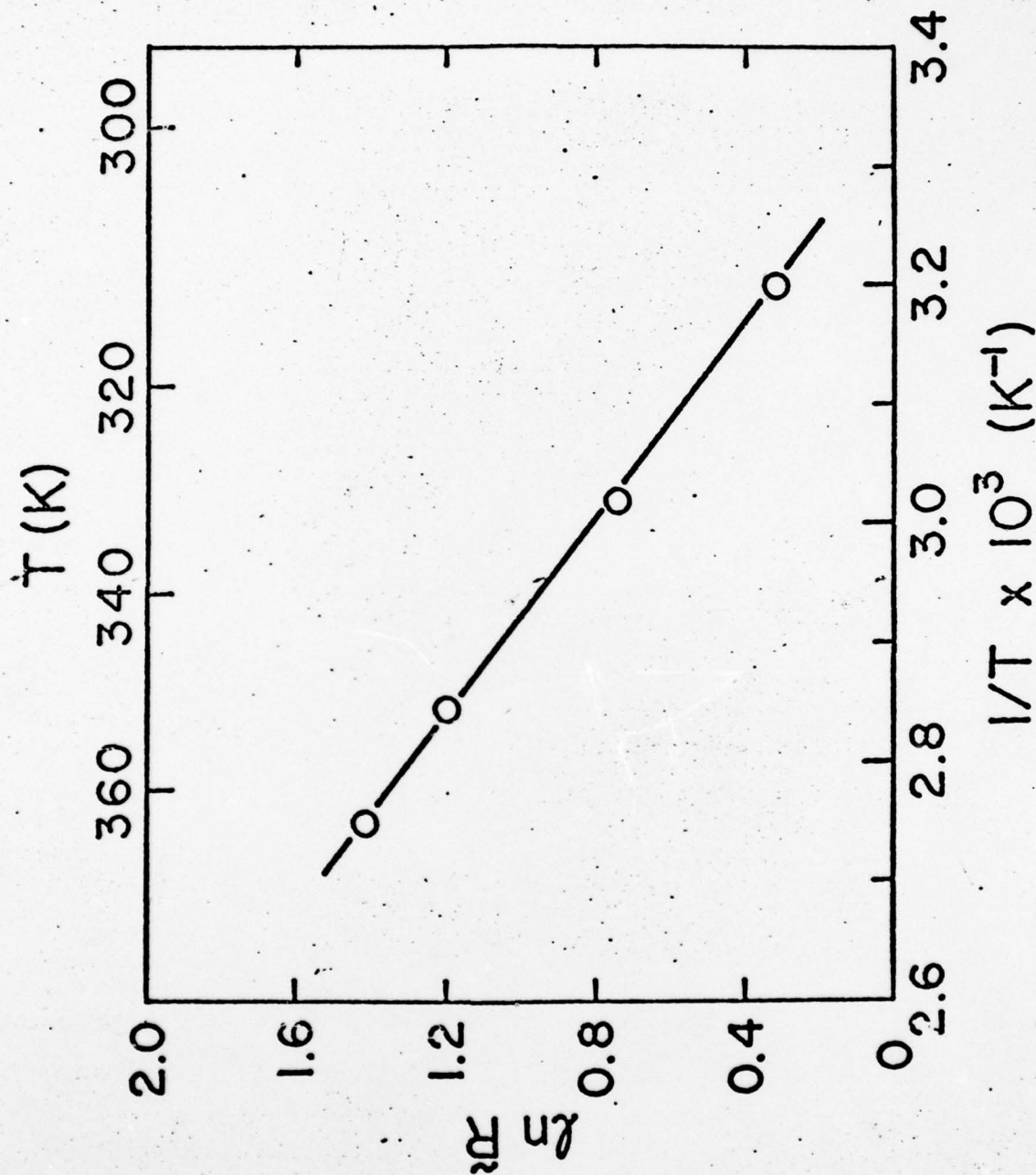


Fig. 3A

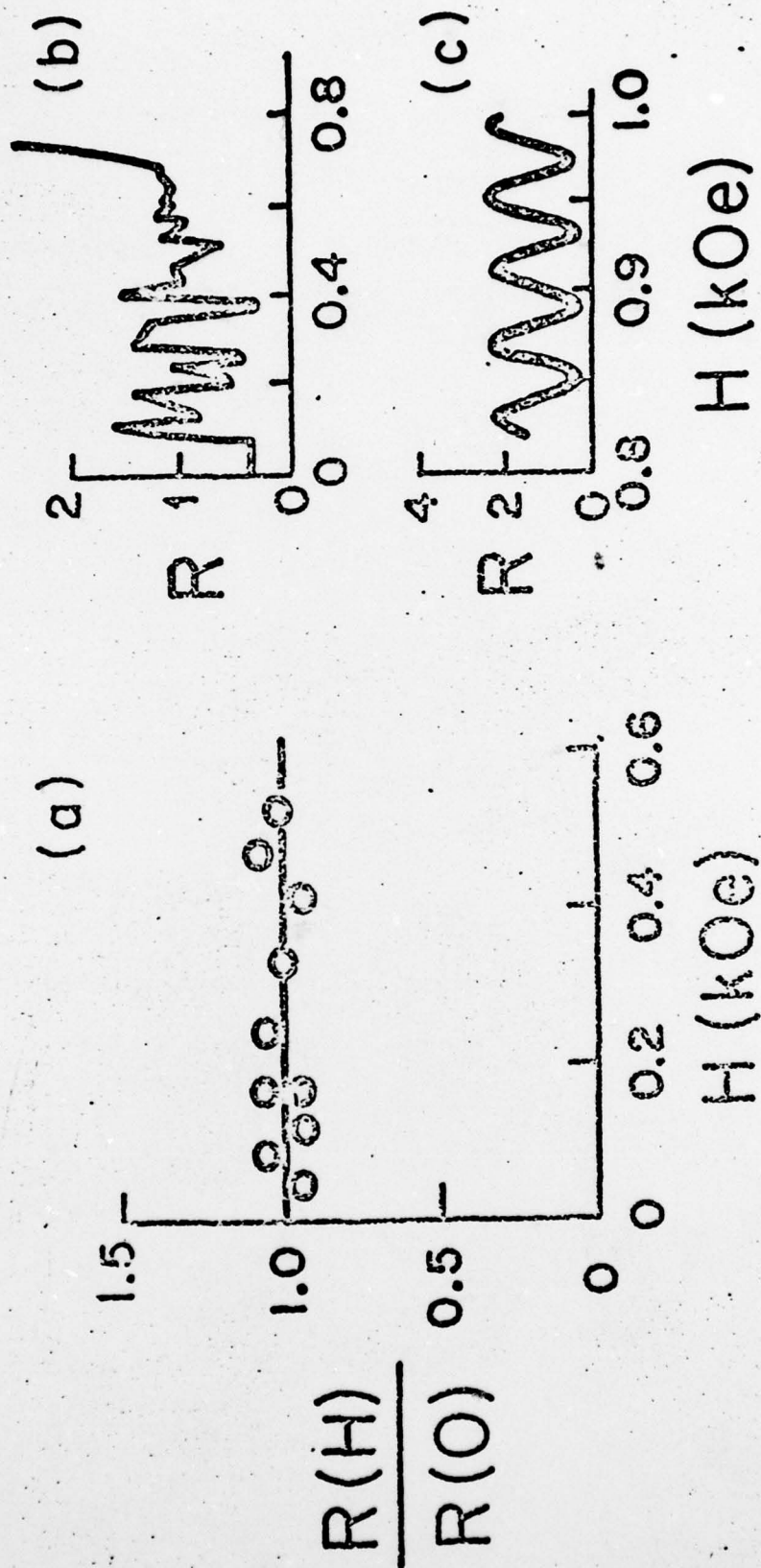


Fig. 4A

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accessible a wide range of Curie temperatures. Our preliminary results on this system show that the ferromagnetic to paramagnetic transition leads to a large change in the activation energy for the carbonylation reaction. Auger measurements confirm that the chemical reaction emphasizes the surface Ni atoms while the activation energy emphasizes the bulk Ni.

